MRI REPORT

ATTACHMENT I

TO

EXHIBIT A

STATEMENT OF WORK

1.0 METHOD FOR PURGEABLE ORGANICS

1.1 Scope and Application

1.1.1 Scope

This method is used for the determination of purgeable (volatile) organics. The complete list of compounds is provided in Table 1.1. The method is complementary to liquid/liquid extraction techniques for extractable organics.

1.1.2 Application

The method is applicable to the measurement of purgeable organics in municipal wastewater sludges. It can be used for screening samples of sludges for purgeable priority organics in surveys of municipal wastewater treatment plants. The method uses GC/MS systems for qualitative and semi-quantitative determination of these compounds.

1.2 Summary

Sludge samples are diluted to 0.5% total solids content with organic-free water. The diluted sample is then purged at room temperature (~ 22°C) with an inert gas for 12 min. Water insoluble compounds boiling below 200°C are transferred from the aqueous phase to the gaseous phase. The gaseous phase is passed through a sorbent trap where the organic compounds

are concentrated. The contents of the trap are then injected into the GC/MS by heating and backflushing the trap. As variations in recovery efficiencies for the individual purgeable organics can be affected by the sample matrices, extensive quality control is required for accurate measurements. The total analysis time including extraction is less than 1 hr. This method is recommended for use only by analysts experienced in the analysis of purgeable organics at the trace levels or by experienced technicians under the close supervision of a qualified analyst.

1.3 Apparatus and Reagents

1.3.1 For Sample Preparation

1.3.1.1 Purge and trap system: Assemble the system as depicted in Figures 1.1 and 1.2. A commercial version, such as the Tekmar Liquid Sample Concentrator Model LSC-1, or its equivalent, may also be used. The purging device is constructed or modified as shown in Figure 1.3. All sample contacting surfaces must be either glass or Teflon. The trap is packed according to Figure 1.4. In order to function properly, the trap must be packed in the following order: Place the glass wool plug in the inlet end of the trap, follow with the OV-1, Tenax, silica gel, charcoal, and finally, the second glass wool plug. Reversing the packing order, i.e., placing the charcoal in the trap first will cause the silica gel and Tenax layers to become contaminated with charcoal dust causing poor desorption

efficiencies. Install the trap so that the effluent from the purging device enters the Tenax end of the trap.

1.3.1.2 Glassware

a. Screw-cap vials - 40 ml with Teflon-lined caps

b. 10 ml, 50 ml, and 100 ml volumetric flasks

1.3.1.3 Analytical balance

1.3.1.4 Roller mill and 1/4 in. stainless steel ball bearings

1.3.1.5 Catalytic gas purifier

1.3.1.6 Purging gas - He or N_2, water compressed, high-purity grade

1.3.1.7 Syringes - 10 µl, 100 l, 1 ml and 5 ml gas-tight for quality control spiking. A large bore 10-ml syringe is used for sample handling. A 20-ml gas-tight syringe is used for preparing standards of neat gaseous compounds.

1.3.1.8 Purgeable - organics-free water. See Section 1.5

a. Activated Carbon-Calgon Filtrasorb-200 or equivalent

1.3.1.9 Trap Packing Materials

a. 3% OV-1 on Chromosorb-W 100/110 mesh

b. Tenax-GC® - 60/80 mesh

c. Silica gel - Davison Grade 15 35/60 mesh or equivalent

d. Coconut charcoal - 26 mesh Barnaby Chaney No. CA-580-26, Lot No. M-2649 or equivalent, as used in NIOSH charcoal adsorption tubes, available through Supelco, Inc. (Cat. No. 2-0267).

1.3.1.10 Glass wool - Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-rinsed glass jar with TFE -lined cap.

1.3.2 For Quantitation and Identification

1.3.2.1 Gas Chromatograph-mass spectrometer data system. Finnigan 4000 or equivalent - The GC/MS interface should be a glass jet separator. The computer system should allow acquisition and storage of repetitive scan data throughout the GC/MS runs. Computer software should be available to allow searching of GC/MS data for display of extracted ion current profiles (EICP) and integration of the peaks. The GC/MS should be fitted with a stainless steel or glass column packed with 0.2% Carbowax 1500 or Carbopack C. Typical column dimensions are 8 ft x 1/8 in. OD stainless steel or 6 ft x 2 mm ID glass.

1.3.2.2 Reference materials - Assayed quantity of compounds of interest, and/or diluted standard solutions of compounds of interest and internal standard compounds in methanol.

1.3.2.3 Mass spectrometer calibration compound - p-fluorobromobenzene.

1.4 Sampling and Preservation

1.4.1 Sampling

Samples must be collected in 40-ml screw-cap vials with zero head space and sealed with Teflon-lined caps. Before using, wash all

sample bottles and TFE seals in detergent, rinse with tap water and finally with distilled water. Allow the bottles and seals to air dry at room temperature, heat in a 105°C oven for 1 hr, then allow to cool in an area known to be free of organics. NOTE: Do not heat the TFE seals for extended periods of time (more than 1 hr) because the silicone layer slowly degrades at 105°C.

1.4.2 Preservation

As a general guideline, ice samples immediately after collection, refrigerate at 4°C, and purge within 10 days. Desorb the trap and complete the analyses immediately after purging.

1.4.3 Solids Determination

The total solids content of the sample is determined in duplicate by weighing two ∿ 1 ml aliquots of the extractable sludge sample before and after drying overnight at 110°C. The general procedure outlined in Standard Methods for the Examination of Water and Wastewater, 14th ed., for the determination of Total Dried Residue (Part 208A) at 103 to 105°C is applicable.

1.5 Preparation of Purgeable Organic-Free Water

Organic-free water is generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon and purged with prepurified N_2, preferably overnight. A Millipore Super-Q Water System or its equivalent may be used to generate organic-free deionized water. Organic-free water can also be prepared by boiling distilled water for 15 min and transferring, while still hot, to a glass-stoppered bottle.

Cool to room temperature. Continuous purging of the organic-free water with pre-purified N_2 may be used during storage to minimize contamination with volatile organic compounds. Test organic-free water daily by analyzing according to this method (see Section 1.9).

1.6 Preparation of Standards

1.6.1 Analytical Standards

Although this protocol assumes the preparation of standard solutions from assayed reference materials, commercially prepared stock solutions, such as Supelco, Inc., Purgeable Standards, may be used for analytical and fortification standards with appropriate dilution.

1.6.1.1 Preparation from neat compounds - From individual assayed reference materials prepare standard stock solutions (at approximately 2 µg/µl) by adding, from a 100-µl syringe, 1 to 2 drops of the 99+% pure reference standard to methanol (9.8 ml) contained in a tared 10-ml volumetric flask (weighed to the nearest 0.1 mg). Add the component so that the two drops fall into the alcohol and do not contact the neck of the flask. (Prepare gaseous standards, i.e., vinyl chloride) in a similar manner using a 20-ml syringe (20 ml) with the gaseous compound. Weight the 10-ml volumetric flask containing 9.8 ml of methyl alcohol to 0.1 mg. Lower the syringe needle to about 5 mm above the methyl alcohol meniscus and slowly inject the standard

into the flask. The gas rapidly dissolves in the methyl alcohol. Reweigh the flask, and use the weight gain to calculate the concentration of the standard. Dilute to volume, mix, and store in the sealed flask. Gas stock standards are generally stable for at least 1 week when maintained at less than 0°C. With the exception of 2-chloroethylvinylether, stock standards of compounds that boil above room temperature are generally stable for at least 4 weeks when stored at 4°C. (Safety Caution: Because of the toxicity of most organohalides, dilutions should be made in a glove box suitable for handling carcinogens. It is advisable to use an approved respirator when high concentrations of such materials must be handled in a fume hood).

From the primary stock solutions, prepare a multicomponent secondary dilution mixture in methyl alcohol at a concentration of 1 µg/ml containing each of the compounds to be determined. Assuming storage at 4°C, prepare a fresh multicomponent secondary dilution mixture on a weekly basis. Daily prepare 10 ml of a 50 ng/ml standard from the 1 µg/ml multicomponent standard by dosing 500 µl into ∿ 9 ml of organic-free water, and adjusting the volume to 10.0 ml. Analyze 1 ml and 5 ml aliquots of the aqueous standard

made up to 10 ml volumes with organic-free water. The resultant analyte concentrations are 5 µg/liter and 25 µg/liter (or 50 ng and 250 ng analyte weights, respectively).

Since reduced sensitivity is frequently observed for the more volatile purgeable compounds, including acrylonitrile, bromomethane, chloromethane, chloroethane, dichlorodifluoromethane, and vinyl chloride, these compounds should be present in the multicomponent standard at higher concentrations. A four-fold increase in the concentrations of bromomethane, chloromethane, chloroethane, dichlorodifluoromethane, and vinyl chloride to produce 4 µg/ml final concentrations of these compounds in the multicomponent secondary dilution will result in more reliable analyte responses. Similarly, a five-fold increase in the acrylonitrile concentration to 5 µg/ml in the multicomponent standard is also desirable.

1.6.1.2 Preparation from commercial mixed stock solutions - As an alternate to the preparation of standards from neat materials, high concentration stock mixtures of volatile organic priority pollutants may be purchased commercially. The method outlined below is specifically designed for utilizing stock mixtures available from Supelco, Inc.

Stock solutions, as received are stored in a freezer when not in use. To prepare a working standard, 25 µl of both Purgeable Standard A and Purgeable Standard B are added to ∿ 99 ml of organic-free water. Subsequently, 100 µl of Purgeable Standard C and 50 µl of the acrolein/acrylonitrile standard are added and the final volume adjusted to 100 ml. Final concentrations for Purgeable A and B compounds are 50 ng/ml. Final concentrations of Purgeable C compounds are 200 ng/ml, and acrolein/acrylonitrile are present at 500 ng/ml in the standard. Analyses of 1 ml and 5 ml of this mixed standard (after volume adjustments to 10 ml with organic-free water), will produce responses nominally corresponding to 50 µg/liter and 250 µg/liter, or 50 ng and 250 ng, respectively..

Prepare a fresh aqueous working standard on a daily basis.

1.6.2 Internal Standard Spiking Solution

Although this protocol assumes the preparation of the standard solutions from neat authentic compounds, appropriate reliable commercial preparations may be used as suitable substitutes.

1.6.2.1 Preparation from neat compounds - From stock standard solutions prepared as above, add a volume of standard to give 1,000 µg each of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane to 45 ml of organic-free water (blank water) contained in a 50-ml volumetric

flask, mix and dilute to volume. Dose 9.0 µl of this internal standard spiking solution into every sample and reference standard analyzed. Prepare a fresh method recovery spiking solution on a weekly basis. Prepare the stock standard solutions monthly, or sooner if deterioration is indicated.

1.6.2.2 Preparation from commercial mixed stock solution - As an alternate to preparation of the mixed internal standard solution from neat compounds, a commercially prepared stock mixture may be employed. The method outlined below is specifically designed for use with the Supelco, Inc., mixed stock internal standard solution which contains 20 mg/ml of each compound.

1.7 Sample Preparation and Purging

1.7.1 Sample Compositing

VOA samples are collected at discrete time intervals by grab sampling. When VOA results for relatively long time intervals, such as 24 hr, are necessary or desirable, compositing of several VOA grab samples must be performed. To do this, normally six VOA grab samples (i.e., one 40-ml grab sample collected every 4 hr over a 24-hr period) will be composited. After storage, sample disruption with a glass stirring rod may be necessary to remove the sample from the VOA vial adequately. Care must be taken to avoid

displacement losses when the stirring rod is used. The chilled samples are mixed with gentle swirling in a 250-ml round-bottom flask. Vigorous mixing must be avoided to prevent analyte losses. Analysis should be performed immediately after compositing. In cases where this is impossible or when sample material is to be retained for future reference, aliquots of the composited VOA samples are returned to VOA vials with zero headspace and refrigerated at 4°C. Normally, only four full VOA vials of composited material can be prepared from six individual grab samples..

1.7.2 Sample Preparation and Purging

Condition the trap at 200°C with a flow of nitrogen or helium. Turn off gas flow to the purging device.

Transfer that amount of sludge which contains greater than 50 mg dry solids (i.e., 1 ml for a 5% sludge) to the syringe body. Assemble the syringe body and plunger. Adjust the sludge aliquot to a volume containing 50 mg dry solids. Add internal standard to the adjusted sample aliquot through the syringe outlet. Transfer the sample to the purging device. Rinse the syringe with organic-free water and add to the purging device. Bring the level in the purging device to the 10-ml mark with organic-free water. Prior to purging, place a glass wool plug in the top of the purge tube to dispense excessive foam. Seal the purging device, and turn on the gas flow to the purging device and adjust to a flow rate of approximately 40 ml/min.

Purge the sample for 12 min while maintaining the sample and trap at room temperature.

1.8 Analysis of the Sample Purge

Analyze the sample purge by GC/MS using the 0.2% Carbowax 1500 on 80/100 mesh Carbopack C column described in Section 1.3.2.1 operated with a He carrier gas flow of 30 ml/min. Heat the trap to 180 to 200°C. Backflush it for 3 min into the gas chromatograph with the oven at 40°C. Hold the oven temperature at 40°C for 3 min during the desorption stage. Immediately after desorption initiate temperature programming. For 8-ft stainless steel columns a programming rate of 10°C/min to 170°C should be used. For 6-ft glass columns a program rate of 6°C/min to 170°C is effective. Hold at this temperature until all compounds of interest have eluted. The purging device must be removed from the instrument and thoroughly rinsed with copious volumes of volatile organic-free water between each sample (nominally three rinses of ∿ 30 ml volume per rinse). Thoroughly clean the purging device according to procedures in Section 1.4.1 between particularly dirty samples. The trap must be conditioned at 180°C with flow for 5 to 7 min between each sample. The MS should be repetitively scanned over the range m/e 20 to 275 at 3 to 5 sec/scan.

1.9 Purgeable Organics Analytical Quality Assurance

In addition to the instrumental quality assurance procedures specified in Sections 1.9.1 and 1.9.2, analyses of replicate and fortified samples and blanks are required to indicate the method precision and accuracy. Since the method precision may be very dependent on the sample matrix, the

1.9.4 Fortified and Duplicate Samples

1.9.4.1 Sample Selection

After the analysis of samples collected at the first sampling time, spike and analyze duplicate sample aliquots from the first samples. For example, for a survey program sampling a POTW plant daily for 4 to 6 days, collect triplicate samples for the first day. After completing analyses of one set of the 1st day samples, spike and analyze duplicate 1st day samples. Spike the 1st day samples using procedures described in Section 1.9.4.2. The frequency of selecting spiked duplicate samples for analysis for sampling programs longer than 6 days should be determined from the detention times of the sludge types samples so as to reflect possible changes in sample matrix.

1.9.4.2 Fortification Procedures

Add one or two stainless steel ball bearings (1/8 in. diameter) to an empty vial and determine the tare weight. Fill the vial with sludge and reweigh; the weight difference determines the wet contents of the vial.

Fortify the sample with all of the compounds noted in Table 1.1 to produce a final concentration two times the concentration found in the unspiked sample, or 10 times the lower limit of detection reported in Table A-1, whichever is

greater. Generally, blanket fortifications of analytes can be accomplished using commercially available mixed standards; however, for analytes present in unusually high concentrations, supplemental fortification with an individual solution may be required. Seal the vial and place on a roller mill in a 4°C cold room; roll the sample for 16 hr before analysis.

The fortified sample is handled as a regular sample during analysis. The quantity of fortified sample analyzed must be equal the quantity of original unfortified sample analyzed.

1.10 Data Handling

Using the characteristic retention times and ions listed in Tables 1.2 and 1.3, obtain extracted ion current profiles (EICPs) of the characteristic ions for each compound. Verify the presence of compounds of interest based on the coincidences of peaks in the characteristic EICPs at the appropriate retention times with intensities in the characteristic ratios.

Calculate the concentrations of compounds identified by comparing the areas of the primary (highest abundance) ion peaks with the areas of the corresponding standard peaks. If the sample matrix produces a significant interference with the primary ion EICP, a secondary ion plot may be used for quantitation. For some analytes, such as toluene and ethylbenzene,

it may be necessary to use ions of substantially lower intensity, e.g., m/e 93 or 107 for quantitative evaluation. Calculate the concentration in the sample as follows:

$$\left(\frac{A}{B}\right)\left(\frac{B_{IS}}{A_{IS}}\right)\left(\frac{N}{V}\right) = \mu g/liter \text{ analyte in wet sludge}$$

where: A = area of peak in sample

B = area of peak in standard

A_{IS} = area of internal standard peak in sample

B_{IS} = area of internal standard peak in standard

N = nanograms in standard

V = volume of wet sludge analyzed (ml)

Table 1.0. Stock VOA Standards Available From Supelco

Purgeable A	Purgeable B	Purgeable C
Dichloromethane	Trifluoromethane	Chloromethane
1,1-Dichloroethylene	trans-1,2-Dichloroethylene	Dichlorodifluoromethane
1,1-Dichloroethane	1,2-Dichloroethane	Bromomethane
Chloroform	1,1,1-Trichloroethane	Vinyl chloride
Carbon tetrachloride	Bromodichloromethane	Chloroethane
1,2-Dichloropropane	trans-1,3-Dichloropropene	
Trichloroethylene	cis-1,3-Dichloropropene	
1,1,2-Trichloroethane	Benzene	
Dibromochloromethane	Bromoform	
Tetrachloroethylene	1,1,2,2-Tetrachloroethane	
	Toluene	
	Ethylbenzene	

Table 1.1. Volatile Organics Detectable With the Purge-And-Trap Method

Compound	Compound
F/Cl/Br/Methanes	**Cl-Ethylenes, Propane**
Methylchloride (chloromethane)	Vinylchloride (chloroethylene)
Methylene chloride (dichloromethane)	1,1-Dichloroethylene (1,1-dichloroethene)
Chloroform (trichloromethane)	Trans-1,2-dichloroethylene (Trans-1,2-dichloroethene)
Carbon tetrachloride (tetrachloromethane)	Trichloroethylene (trichloroethene)
Methylbromide (bromomethane)	Tetrachloroethylene (tetrachloroethene)
Bromoform (tribromomethane)	1,2-dichloropropane
Chlorodibromomethane	1,2-dichloropropylene
Bromodichloromethane	Trans-1,3-dichloropropene
Dichlorodifluoromethane	Cis-1,3-dichloropene
Trichlorofluoromethane	
Cl-Ethanes	**Alkenes**
Chloroethane	Acrolein (propenal)
1,1-Dichloroethane	Acrylonitrile (propene nitrile)
1,2-Dichloroethane	
1,1,1-Trichloroethane	**Ethers**
1,1,2-Trichloroethane	
1,1,2,2-Tetrachloroethane	Bis-chloromethylether* (sym.-dichlorodimethylether)
Cl-Benzenes	2-Chloroethylvinylether (2-chloroethyl ethenylether)
Benzene	Bis-(2-chloroethyl) ether (β,β'-dichlorodiethylether)
Chlorobenzene	Bis-(2-chloroisopropyl) ether (β,β'-dichlorodisopropyl ether)
Toluene	
Ethylbenzene	

* Bis-Chloromethylether has a half-life of about 10 seconds in aqueous mixtures.

Table 1.2. Elution Order of Volatile Priority Pollutants[a/]

Compound	RRT[b/]
Chloromethane	0.152
Dichlorodifluoromethane	0.172
Bromomethane	0.181
Vinyl Chloride	0.186
Chloroethane	0.204
Methylene Chloride	0.292
Trichlorofluoromethane	0.372
1,1-Dichloroethylene	0.380
Bromochloromethane (IS)	0.457
1,1-Dichloroethane	0.469
Trans-1,2-dichloroethylene	0.493
Chloroform	0.557
1,2-Dichloroethane	0.600
1,1,1-Trichloroethane	0.672
Carbon Tetrachloride	0.684
Bromodichloromethane	0.750
Bis-chloromethyl ether	0.760
1,2-Dichloropropane	0.818
Trans-1,3-dichloropropene	0.847
Trichloroethylene	0.867
Dibromochloromethane	0.931
Cis-1,3-dichloropropene	0.913
1,1,2-Trichloroethane	0.913
Benzene	0.937
2-Chloroethylvinyl ether	0.992
2-Bromo-1-chloropropane (IS)	1.000
Bromoform	1.115
1,1,2,2-Tetrachloroethene	1.262
1,1,2,2-Tetrachloroethane	1.281
1,4-Dichlorobutane (IS)	1.312
Toluene	1.341
Chlorobenzene	1.489
Ethylbenzene	1.814
Acrolein	Unknown
Acrylonitrile	Unknown

a/ These data were obtained under the following conditions: GC column - stainless steel, 8-ft long x 0.1 in. I.D. packed with Carbopack C (60/80 mesh), coated with 0.2% Carbowax 1500; carrier flow - 30 ml/min; oven temperature - initial 60°C held for 3 min, programmed 8°C/min to 160°C and held until all compounds eluted.

b/ Retention times relative to 2-bromo-1-chloropropane with an absolute retention time of 829 sec.

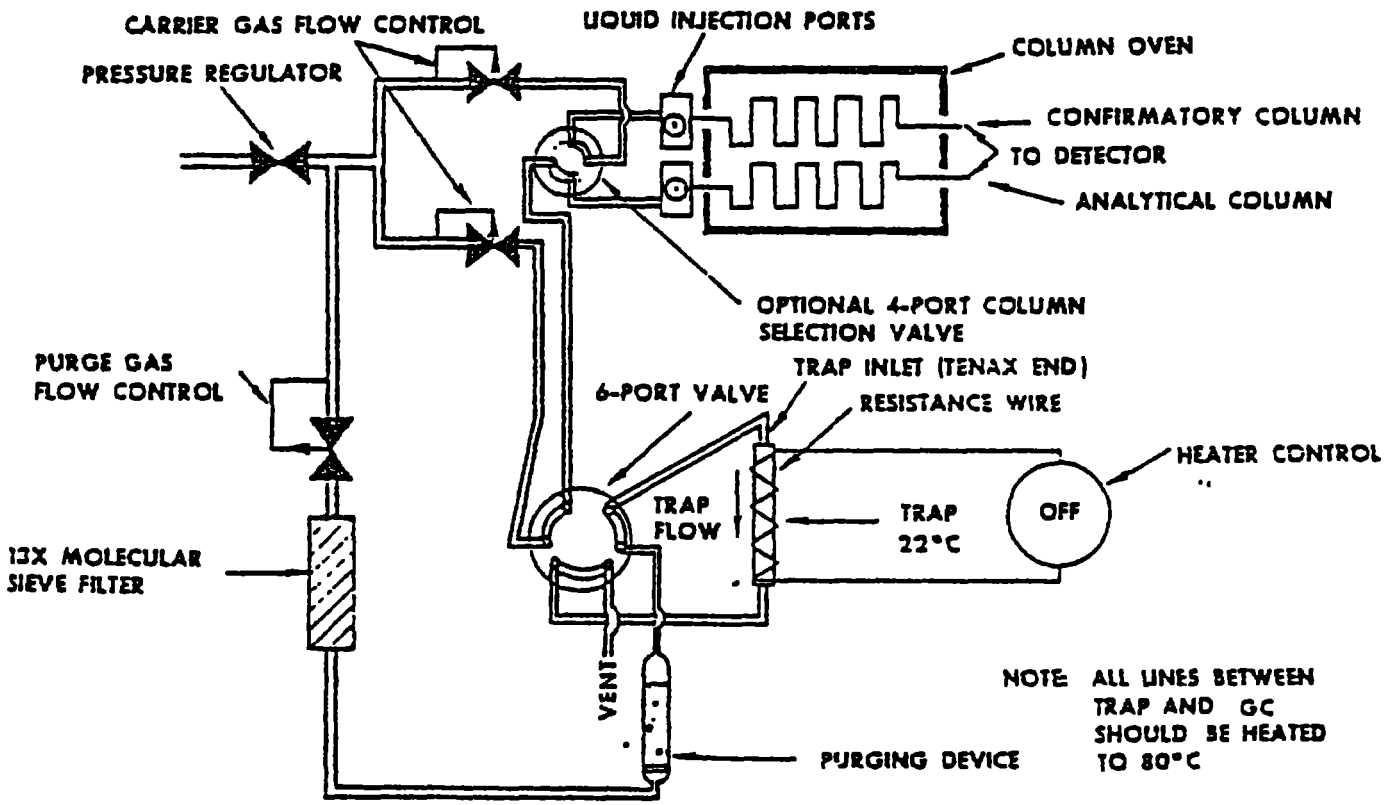

Figure 1.1 - Schematic of Purge and Trap Device - Purge Mode

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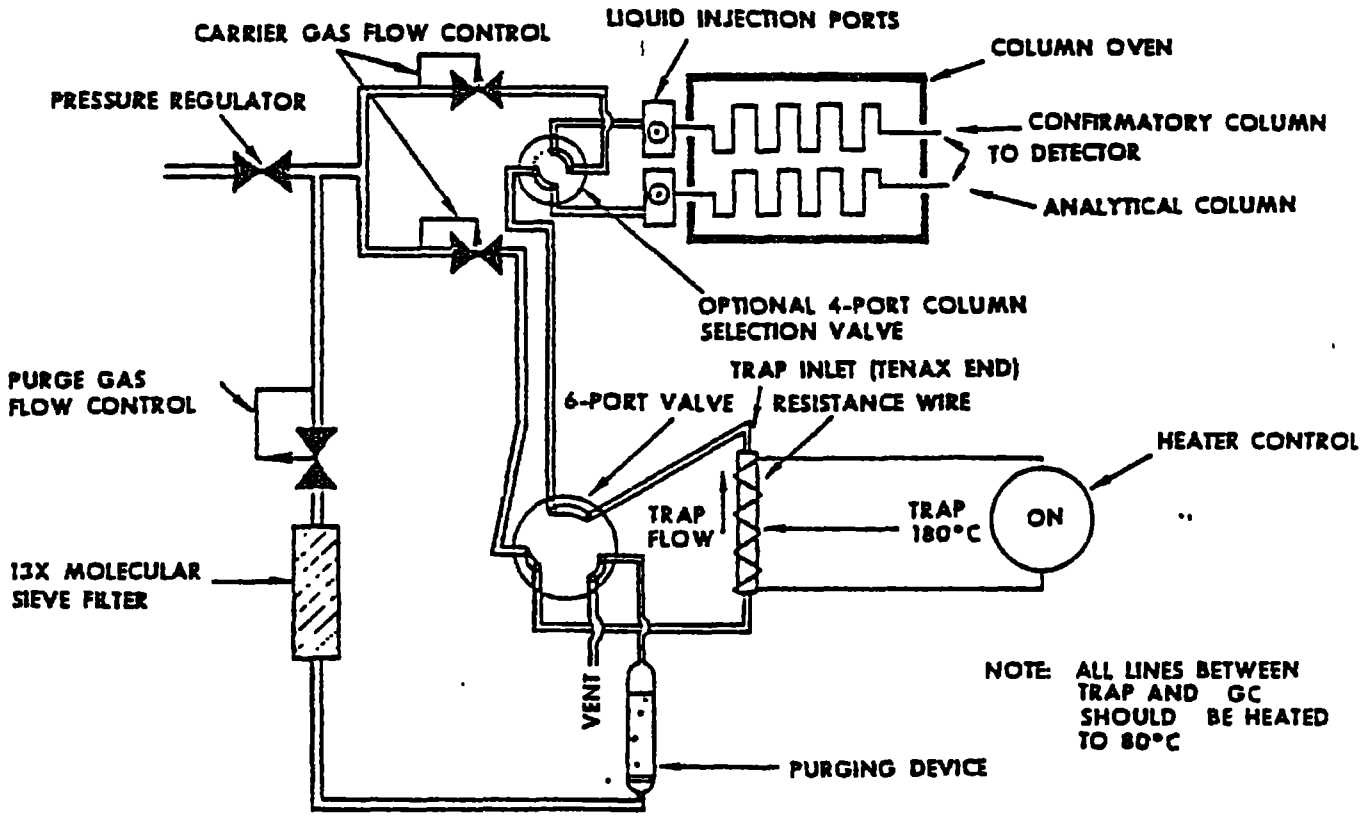

Figure 1.2 - Schematic of Purge and Trap Device - Desorb Mode

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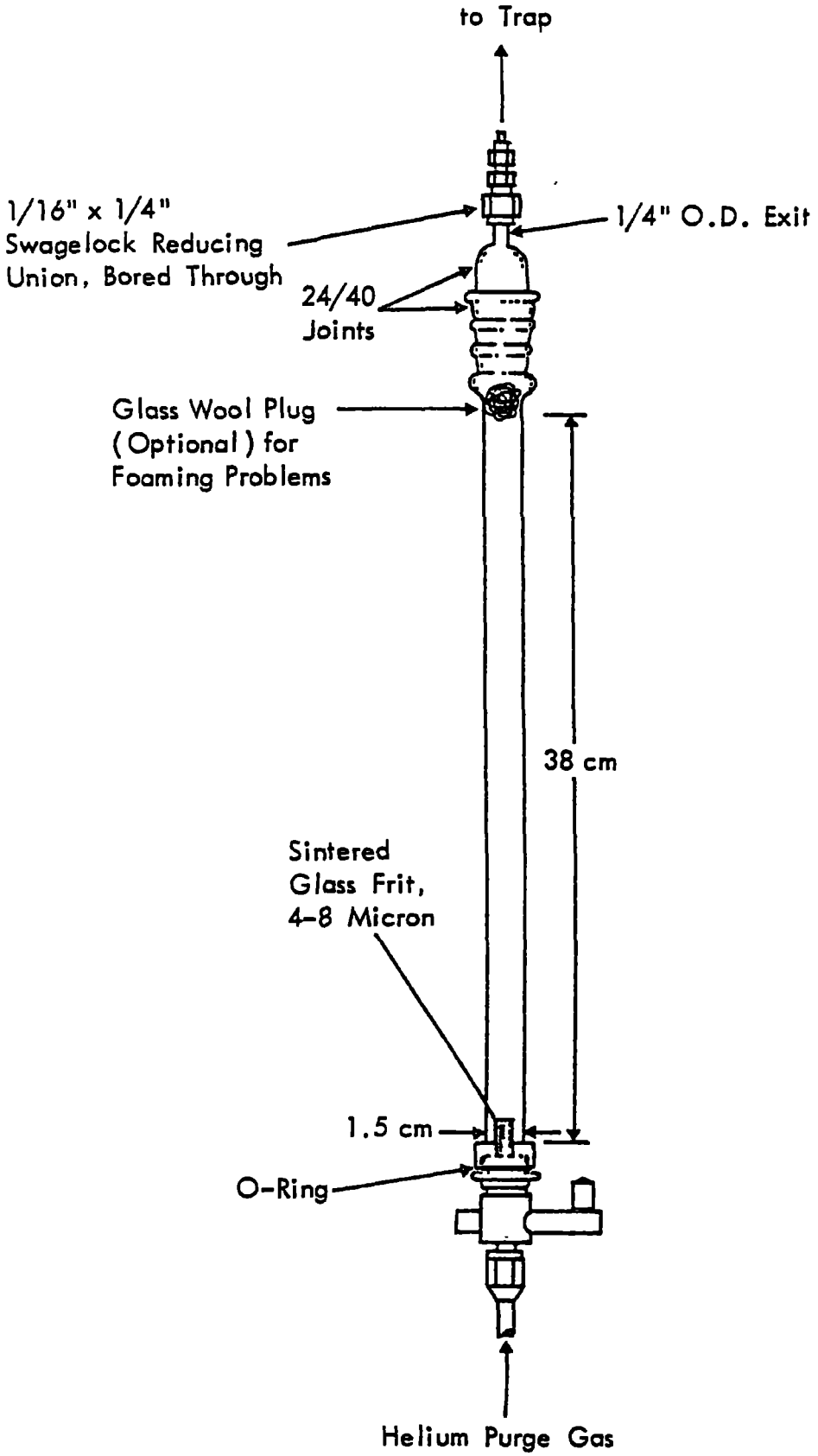

Figure 1.3 - Sludge Purging Tube

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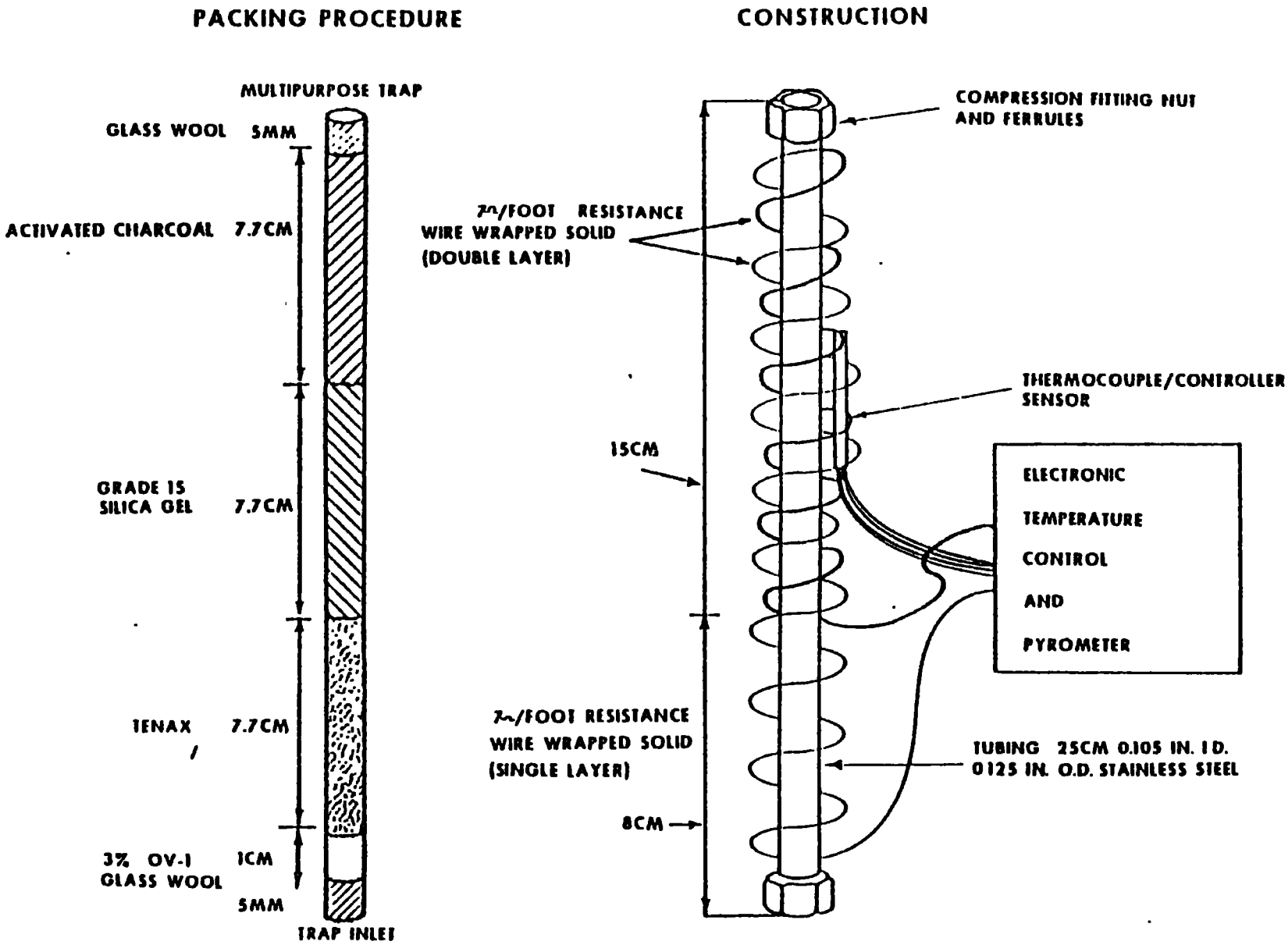

Figure 1.4 - Trap Packings and Construction

Table 1.3. Characteristic Ions of Volatile Organics

Compound	EI Ions (Relative Intensity)	Ion Used to Quantify
Chloromethane	50(100); 52(33)	50
Dichlorodifluoromethane	85(100); 87(33); 101(13); 103(9)	101
Bromomethane	94(100); 96(94)	94
Vinyl chloride	62(100); 64(33)	62
Chloroethane	64(100); 66(33)	64
Methylene chloride	49(100); 51(33); 84(86); 86(55)	84
Trichlorofluoromethane	101(100); 103(66)	101
1,1-Dichloroethylene	61(100); 96(80); 98(53)	96
Bromochloromethane (IS)	49(100); 130(88); 128(70); 51(33)	128
1,1-Dichloroethane	63(100); 65(33); 83(13); 85(8); 98(7); 100(4)	63
Trans-1,2-dichloroethylene	64(100); 96(90); 98(57)	96
Chloroform	83(100); 85(66)	83
1,2-Dichloroethane	62(100); 64(33); 98(23); 100(15)	98
1,1,1,-Trichloroethane	98(100); 99(66); 117(17); 119(16)	97
Carbon tetrachloride	117(100); 119(96); 121(30)	117
Bromodichloromethane	83(100); 85(66); 127(13); 129(17)	127
Bis-chloromethyl ether	79(100); 81(33)	79
1,2-Dichloropropane	63(100); 65(33); 112(4); 114(3)	112
Trans-1,3-Dichloropropene	75(100); 77(33)	75
Trichloroethylene	95(100); 97(66); 130(90); 132(85)	130
Dibromochloromethane	129(100); 127(78); 208(13); 206(10)	127
cis-1,3-Dichloropropene	75(100); 77(33)	75
1,1,2-Trichloroethane	83(95); 85(60); 97(100); 99(63); 132(9); 134(8)	97
Benzene	78(100)	78
2-Chloroethylvinyl ether	63(95); 65(32); 106(18)	106
2-Bromo-1-chloropropane (IS)	77(100); 79(33); 156(5)	77
Bromoform	171(50); 173(100); 175(50); 250(4); 252(11); 254(11); 256(4)	173
1,1,2,2-Tetrachloroethene	129(64); 131(62); 164(78); 166(100)	164
1,1,2,2-Tetrachloroethane	83(100); 85(66); 131(7); 133(7); 166(5); 168(6)	168
1,4-dichlorobutane (IS)	55(100); 90(30); 92(10)	55
Toluene	91(100); 92(78)	92
Chlorobenzene	112(100); 114(33)	112
Ethylbenzene	91(100); 106(33)	106
Acrolein	26(49); 27(100); 55(64); 56(83)	56
Acrylonitrile	26(100); 51(32); 52(75); 53(99)	53

Table 1.4. p-Fluorobromobenzene Ions and Ion Abundance Criteria

M/E	Ion Abundance Criteria
50	20-40% of base peak
75	55-75% of base peak
95	base peak
174	75-98% of base peak
175	5-9% of m/e 174
176	75-98% of base peak and 93-99% of m/e 174
177	0-5% of m/e 176

2.3 Apparatus

2.3.1 For sampling, extraction and

2.3.1.1 Emulsifier-Tekmar Ti su

2.3.1.2 Centrifuge.

2.3.1.3 Centrifuge tubes wit
larger capacity.

2.3.1.4 Kuderna-Danish (K-D) 31

a. Snyder Columns -

b. Evaporating flas

c. Receiver Ampuls - 1
attachment.

2.3.1.5 Water or steam bath

2.3.1.6 Chromatographic (dry: g
ID) without a fritte p

2.3.1.7 Separatory funnels -

2.3.1.8 Syringe - 100 ml, Py: x

2.3.1.9 Graduated cylinder - 0

2.3.1.10 Vials - 1 dram (~ 4 m

2.3.1.11 Sample bottles - 1,00
screw caps.

2.3.1.12 GPC - Analytical Bioc
1002 or equivalent wi
60 g of BioBeads SX-3

2.3.1.13 Syringe filter holde
4310, or equivalent.

2.3

2.4.2 de

2.4 Reag nt

2.4.

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2.0 METHOD FOR SEMIVOLATILE ORGANICS

2.1 Scope and Application

2.1.1 Scope

This method applies to the determination of the base, neutral, and acid-extractable organic compounds as described in Table 2.1.

2.1.2 Application

The method is for the measurement of these compounds in municipal wastewater sludges. It can be used as a qualitative and semiquantitative screening procedure for the analyses of priority toxic organics in surveys of sludges from municipal wastewater treatment plants. As a screening tool, the procedure requires the use of a GC/MS spectrometer as the final detector.

2.2 Summary

2.2.1 This method (Figure 2.1) uses wet sludge/solvent extraction aided by a high-speed homogenizer. The extract is separated by centrifugation and removed with a pipette. Sludges are extracted at pH ≥ 11 and again at pH ≤ 2 to extract base/neutral and acidic compounds, respectively. Both extracts are cleaned by gel permeation chromatography (GPC) and semivolatile organic priority pollutants are determined in the cleaned extracts by GC/MS.

The method is recommended for use only by experienced organic analysts or by competent personnel under the close supervision of an experienced organic analyst.

2.5 Preparation of Standards

Primary standard solutions may be prepared from the pure compounds by dissolving 10 mg quantities into 10.0 ml of dichloromethane. Mixed analytical standards may be prepared by diluting the primary solutions. Analytical standards for all semivolatile compounds should be prepared in three solutions. The acids standard should contain each of the phenolic compounds at concentrations in the range of 50 to 200 ng/µl. B/N/P compounds should be split between two solutions, both at concentrations in the range of 20 to 100 ng/µl. One standard should contain the more unstable B/N compounds listed in Table 2.2 and the second should contain the remaining B/N/P compounds. Analytical standards may also be obtained from EPA Effluent Guidelines Division or be prepared by dilution of stock standard solutions purchased from chromatographic materials suppliers such as Supelco, Inc. All working standards must include D-10-anthracene at 20 ng/µl.

2.6 Sampling and Preservation

2.6.1 Sampling

Samples must be collected in glass containers (1,000-4,000 ml) with a TFE-lined cap. The container should be prewashed with acetone and dried before use. Containers should be filled no more than two-thirds full with sample to minimize breakage during freezing.

2.6.2 Preservation

Preferably, samples should be iced or refrigerated at 4°C for not more than 24 hours before extraction. Where extraction cannot be performed within 24 hours, samples should be frozen. Samples may be stored for up to 30 days at -20°C or indefinitely at -75°C. In order to prevent breakage during storage, the containers should not be slightly warmed and then recooled. The iced or defrosted sample should be homogenized by mixing for 1 minute with a tissuemizer before analysis.

2.7 Sample Extraction

2.7.1 Preparation of Drying Column

Immediately prior to extracting a sample, prepare a drying tube for the extract. Place a small glass wool plug in the bottom of the column and add anhydrous sodium sulfate to a depth of 10 to 15 cm.

2.7.2 pH Adjustment

Thoroughly mix the sludge sample by homogenizing in the sample bottle for 1 minute, 4 samples at a time, then quickly remove an 80 ml aliquot into a 100 ml graduated cylinder. Transfer the aliquot into a 250 ml centrifuge tube. Basify the 80 ml portion to pH ≥ 11 with 6 N sodium hydroxide solution. Mix briefly with the homogenizer to insure uniform sample pH.

(Note: If copious precipitation of carbonates is observed when sodium hydroxide is added, make the sample slightly acidic with

6 N hydrochloric acid and allow the carbon dioxide evolution to cease before basifying the sample.)

2.7.3 Extraction

Add 80 ml of dichloromethane to the sample and homogenize for 45 to 60 sec. Do not homogenize more than 60 sec to avoid heating the sample. Centrifuge the samples and extracts at 3,000 rpm for 30 minutes. Repeat centrifugation if satisfactory phase separation is not achieved. The mixture will separate into an aqueous layer over the dichloromethane extract with a solids cake at the water-dichloromethane interface. Withdraw the extract from each centrifuge tube with a 100 ml pipette. Discharge the extracts into a 500 ml separatory funnel. Drain the dichloromethane through the drying column into a Kuderna-Danish evaporator. Retain any aqueous layer and return it in approximately equal volumes to each of the four centrifuge tubes.

Extract the sample two more times (to achieve three-fold extraction) according to procedures described in Sections 2.7.3 and 2.7.4. Wash the drying column with an additional 100 ml of dichloromethane and combine the eluent with the extracts.

2.7.4 Extract Concentration

Add a boiling chip to the extract in the Kuderna-Danish evaporator and concentrate the extract to ∿ 8 ml using a 85°C water bath or a steam bath. If the extract is only slightly colored and not viscous

concentrate it further to 5 ml. If the extract solidifies after cooling, dilute it to 8 ml. Transfer the extract to a 10 ml volumetric flask (or 10 ml graduated tube), dilute to the mark and store at 4°C for GPC cleanup.

2.7.5 Acidic Extraction

Acidify the sludge sample portions to pH ≤ 2 with 6 N hydrochloric acid and extract the sample again by procedures described in Sections 2.7.3 to 2.7.4. Discard the extracted sludge aliquots.

2.8 Extract Cleanup

2.8.1 GPC Setup and Calibration

2.8.1.1 Packing the column - Place 50 to 60 g of Bio Beads SX-3 in a 400 ml beaker. Cover the beads with dichloromethane and allow the beads to swell overnight (before packing the columns). Transfer the swelled beads to the column and start pumping solvent through the column, from bottom to to top, at 5.0 ml/min. After ~1 hour, adjust the pressure on the column to 7 to 10 psi and pump an additional 4 hours to remove air from the column. Adjust the column pressure periodically as required to maintain 7 to 10 psi.

2.8.1.2 Calibration of the column - Load 5 ml of the corn oil solution into sample loop No. 1 and 5 ml of the phthalate-phenol solution into loop No. 2. Inject the corn oil and collect 10 ml fractions (i.e., change fraction at 2 minute

intervals) for 36 minutes. Inject the phthalate-phenol solution and collect 10 ml fractions for 60 minutes. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue. Analyze the phthalate-phenol fractions by GC/FID on the SP-2250 and SP-1240-DA columns. Plot the concentration of each component in each fraction versus total eluent volume (or time) from the injection points. Choose a "dump time" which allows ≥85% removal of the corn oil and ≥85% recovery of the bis(2-ethylhexyl)-phthalate. Choose the "collect time" to extend at least 10 minutes after the elution of pentachlorophenol. "Wash" the column 20 minutes between samples. Typical parameters selected are: dump time, 20 minutes (100 ml), collect time, 30 minutes (150 ml), and wash time, 20 minutes (100 ml). The column can also be calibrated by the use of a 254 nm UV detector in place of gravimetric and GC analyses of fractions. Measure the peak areas at various elution times to determine appropriate fractions.

2.8.2 Operation

Prefilter or load all extracts via the filter holder to avoid particulates that might cause flow stoppage. Load one 5.0 ml aliquot for extracts of 10 ml volume. Purge the sample loading

tubing thoroughly with solvent between extracts. After especially dirty extracts, run a GPC blank (i.e., dichloromethane) to check for carry-over. Process the extracts using the dump, collect, and wash parameters determined from the calibration and collect the cleaned extracts in 500 ml brown bottles. Concentrate the cleaned extracts, combining collected fractions from multiple injections, to ∿ 10 ml using Kuderna-Danish evaporators and then to ∿ 3 ml using micro Snyder columns. Transfer the cleaned extracts to 10 ml graduated tubes and dilute to 5.0 ml with dichloromethane. Store at 4°C for GC/MS analysis. Intensely colored extracts may require a second GPC cleanup.

2.9 Sample Extract Analysis

2.9.1 Acid Extracts

GC/MS analysis - Analyze acid extracts by GC/MS using the SP-1240-DA column described in Section 2.3.2.1, operated under the following conditions:

Column temperature - 85°C for 4 minutes, 85 to 200°C at 10°C/min and 200°C until after the elution time for 4-nitrophenol.

Injector temperature - 185°C

GC/MS interface temperature - 275°C

Carrier gas - Helium at 30 ml/min

Injection size - 2 µl

The MS should be repetitively scanned over the range m/e 40 to 475 at 3 sec/scan. Immediately prior to analysis, spike each extract with 50.0 µl of the internal standard solution of 2.0 µg/µl D-10-anthracene in dichloromethane.

2.9.2 Base/Neutral Pesticide Extracts

GC/MS analysis - Analyze the B/N/P extracts by GC/MS using the SP-2250 column described in Section 2.3.2.1 operated under the following conditions:

Column temperature - 50°C for 4 minutes, 50 to 260°C at 10°C/min, and 260°C until after the elution time for benz[g,h,i]perylene.

Injector temperature - 225°C

GC/MS interface temperature - 275°C

Carrier gas - Helium at 30 ml/min

Injection size - 2 µl

The MS should be repetitively scanned over the range m/e 40 to 475 at 3 sec/scan.

Immediately prior to analysis, spike each extract with 50.0 µl of the internal standard solution, which contains 2.0 µg/µl D-10-anthracene in dichloromethane.

2.10 Extractable Organics Analytical Quality Assurance

In addition to the instrumental quality assurance procedures specified in Sections 2.10.1 and 2.10.2, analyses of replicate and fortified samples and blanks are required to indicate the method precision and accuracy. Since the method precision may be very dependent on the sample matrix, the frequency and selection of replicate and fortified samples, method and field blanks, and fortified blanks is designed to provide some precision and accuracy data for each sample matrix encountered and is consistent with the objectives and limitations of screening analyses.

2.10.1 Method Blanks

Analyze one method blank (i.e., organic-free water) and one method blank spiked with each of the representative semivolatile compounds at 10 times the detection limits for every 15 samples analyzed or at least once each month that analyses are being conducted. Method blanks and spiked blanks are extracted and the extracts cleaned by the same procedures used for samples. Analyze extracts of spiked blanks by the GC/MS procedures described in Section 2.0. Analyze extracts of blanks by GC/FID using the same chromatographic columns and conditions. Analyze all blank extracts by GC/MS that exhibit peaks more intense than the D-10-anthracene internal standard.

2.10.2 Analytical Standards

2.10.2.1 Acidic Compounds

2.10.2.2 Analytical Quality Assurance

2.10.2.2.a Analyze daily a GC/MS quality assurance solution containing 10 ng/µl decafluorotriphenylphosphine (DFTPP), and 20 ng/µl of D-10-anthracene and 50 ng/µl 4-nitrophenol. Detection of 4-nitrophenol and the acceptability of the DFTPP spectrum quality, based on the ion abundance standards outlined in Table 2.3, are necessary criteria for proceeding with sample extract analyses.

2.10.2.2.b Analyze daily a standard solution containing each of the acidic compounds listed in Table 2.1 in the concentration range of 50 to 200 ng/µl plus D-10-anthracene at 20 ng/µl. Response factor data obtained from these standards are used to estimate the concentrations of compounds identified in sample extracts.

2.10.2.3 Base/Neutral and Pesticide Compounds

2.10.2.3.a Analyze daily a GC/MS quality assurance solution containing 10 ng/µl DFTPP, 20 ng/µl D-10-anthracene, and 50 ng/µl benzidene. Detection of benzidene and the acceptability

of the DFTPP spectrum quality (see Table 2.3) are necessary criteria for proceeding with sample extract analyses.

2.10.2.3.b Analyze daily standard solutions containing the base/neutral and pesticide compounds listed in Table 2.1 in the concentration range of 20 to 100 ng/µl plus D-10-anthraceene at 20 ng/µl. Response factor data obtained from these standards are used to estimate the concentrations of compounds identified in sample extracts.

2.10.3 Field Blanks

Extract an 80 ml aliquot of each field blank by bech extraction with 3 100 ml portions of dichloromethane in a 1,000 ml separatory funnel. Dry the extract by passage through a short column of anhydrous Na_2SO_4 and concentrate to 1.0 ml in a Kuderna-Danish evaporator. Analyze field blank extracts by GC/FID using the chromatographic columns and conditions described in Section 2.0. Analyze all blank extracts by GC/MS that exhibit peaks more intense than the D-10-anthracene internal standard.

2.10.4 Fortified and Duplicate Samples

2.10.4.1 Sample Selection - After the analysis of samples collected at the first sampling time, spike and analyze duplicate sample aliquots from the first samples. For example,

for a survey program sampling a POTW plant daily for 4 to 6 days, collect triplicate samples for the first day. After completing analyses of one set of the first day samples, spike and analyze duplicate first day samples. Spike the first day samples using procedures described in Section 2.10.4.2. The frequency of selecting spiked duplicate samples for analysis for sampling programs longer than 6 days should be determined from the detention times of the sludge types sampled so as to reflect possible changes in sample matrix.

2.10.4.2 Fortification Procedures - Spike an 80 ml aliquot of sludge with all of the compounds identified in the sample and the representative semivolatile compounds listed in Table 3.2 to produce a final concentration that is two times the observed concentration or 10 times the lower limit of detection reported in Table 2.9, whichever is greater. The spike should be contained in two acetone solutions. The first contains acidic and neutral compounds and the second contains basic compounds. The concentrations of the spiking solutions should be such that 1 to 5 ml of each solution are added to the sludge sample. Homogenize the spiked sample for 45 to 60 sec and store at 4°C overnight before extraction and analysis.

2.11 Data Handling

Using the characteristic retention times and ions listed in Tables 2.4 to 2.6, obtian EICP's of the characteristic ions for each compound. Verify the presence of the compounds of interest based on the coincidences of peaks in the characteristic EICPs at the appropriate retention times with intensities in the characteristic ratios. Calculate the concentrations of compounds identified by comparing the areas of the primary (highest abundance) ion EICP peaks with the areas of the corresponding standard peaks. If the sample matrix produces a significant interference with the primary ion EICP, a secondary ion EICP may be used for quantitation. Calculate the concentration of compounds identified in the sample as follows:

$$\left(\frac{A}{B}\right)\left(\frac{B_{IS}}{A_{IS}}\right)\left(\frac{V_E}{V_1}\right)\left(\frac{N}{V_S}\right)\left(\frac{1}{F}\right) = \text{µg/liter of analyte in wet sludge}$$

where:

A = area of peak in sample extract

B = area of peak in standard

A_{IS} = area of internal standard peak in sample extract

B_{IS} = area of internal standard peak in standard

V_1 = volume of extract injected (µl)

V_E = total volume of extract (ml)

N = nanograms in standard

V_S = volume of wet sludge extracted (l)

F = fraction of extract cleaned by GPC for analysis (e.g., $\frac{20\ ml}{25\ ml} = .8$).

007501

Table 2.1. Semivolatile Organic Priority Pollutants

ACIDS

4-Chloro-3-methylphenol
2-Chlorophenol
2,4-Dichlorophenol
2,4-Dimethylphenol
4,6-Dinitro-2-methylphenol
2-Nitrophenol
4-Nitrophenol
Pentachlorophenol
Phenol
2,4,6-Trichlorophenol

BASES

Benzidine
3,3'-Dichlorobenzidine

NEUTRALS

Polycyclic Aromatic Hydrocarbons

Acenaphthene
Acenaphtylene
Anthracene
Benzo(a)anthracene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Benzo(a)pyrene
Chrysene
Dibenzo(a,g)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

Phthalates

Bis(2-ethylhexyl) phthalate
Butylbenzyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-butyl phthalate
Di-n-octyl phthalate

Chlorinated Hydrocarbons

2-Chloronaphthalene
1,2-Dichlorobenzene
1,3-Dcihlorobenzene
1,4-Dichlorobenzene
Hexachlorobenzene
Hexachloro-1,3-butadiene
Hexachloroethane
Hexachlorocyclopentadiene
1,2,5-Trichlorobenzene

Chloroalkyl Ethers

Bis-(2-chloroethyl) ether
Bis-(2-chloroethoxy)methane
Bis-(2-chloroisopropyl) ether
2-Chloroethyl vinyl ether

Table 2.1 (Concluded)

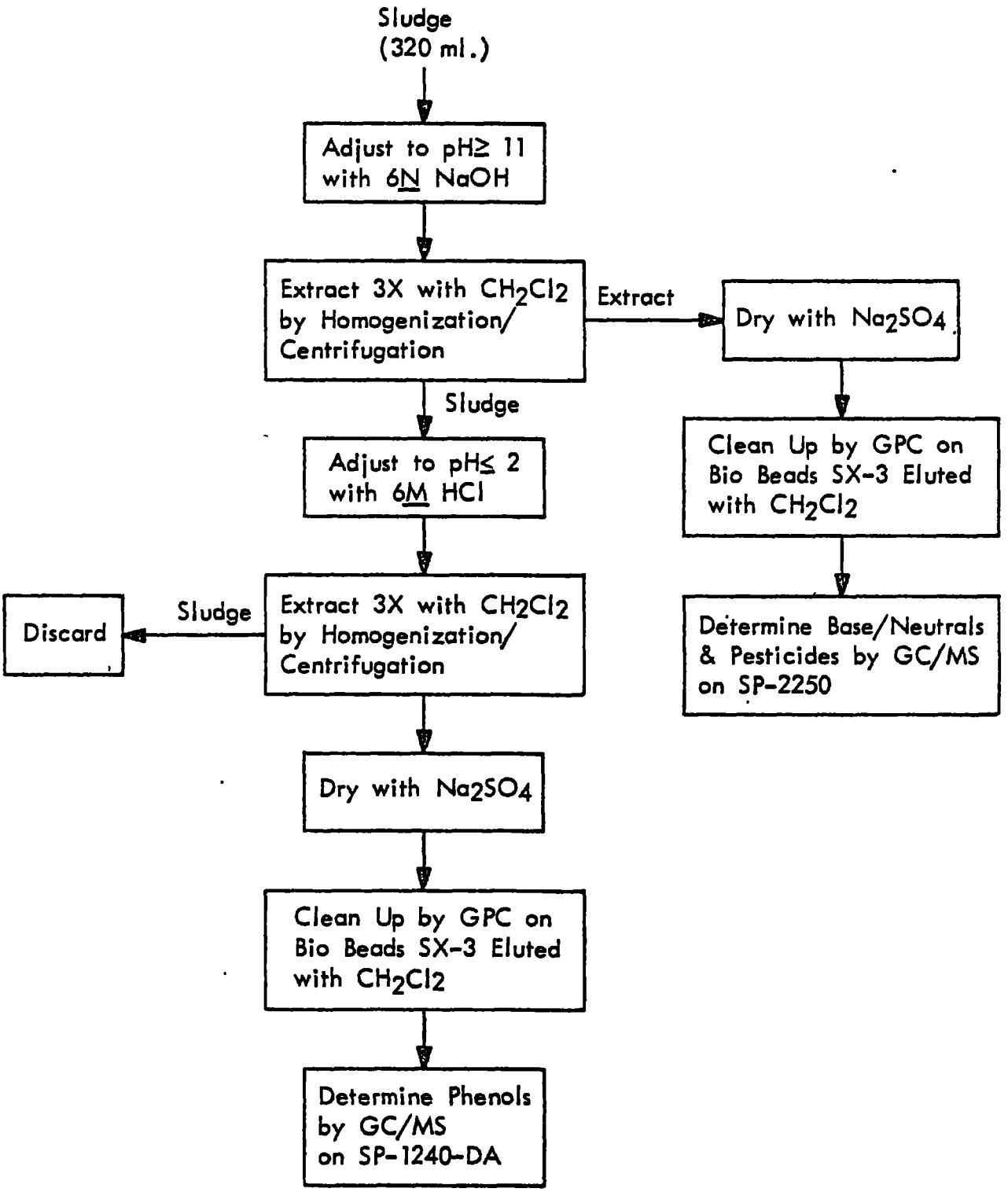
NEUTRALS

Miscellaneous Neutrals

4-Bromophenyl phenyl ether
4-Chlorophenyl phenyl ether
2,4-Dinitrotoluene
N-Nitrosodiethylamine
N-Nitrosodimethylamine
2,6-Dinitrotoluene
Isophorone
Nitrobenzene
N-Nitrosodiphenylamine

PESTICIDES

β-Endosulfan
α-BHC
γ-BHC
β-BHC
Aldrin
Heptachlor
Heptachlor epoxide
α-Endosulfan
Dieldrin
4,4'-DDE
4,4'-DDD
4,4'-DDT
Endrin
Endosulfan sulfate
δ-BHC
Chlordane
Toxaphene
PCB-1242
PCB-1254



Analysis Scheme for Semivolatile Organics

007504

Table 2.2. Unstable B/N Compounds

bis(2-Chloroisopropyl) ether
Nitrobenzene
N-Nitroso-di-n-propylamine
bis(2-Chloroethoxy) methane
Isophorone
2,6-Dinitrotoluene
2,4-Dinitrotoluene
1,2-Diphenylhydrazine
Benzidine
3,3'-Dichlorobenzidine
N-Nitrosodimethylamine

Table 2.3. DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	less than 2% of mass 69
70	less than 2% of mass 69
127	40-60% of mass 198
197	less than 1% of mass 198
198	base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	1% of mass 198
441	less than mass 443
442	greater than 40% of mass 198
443	17-23% of mass 442

007505

Table 2.4. Acid Compounds

Compound Name	RRT[a/] D-10-Anthracene	Characteristic El Ions (Rel. Int.)
2-Chlorophenol	0.38	128(100), 64(54), 130(31)
2-Nitrophenol	0.43	139(100); 65(35), 109(8)
Phenol	0.50	94(100), 65(17), 66(19)
2,4-Dimethyl phenol	0.58	122(100), 107(90), 121(55)
2,4-Dichlorophenol	0.60	162(100), 164(50), 98(61)
2,4,6-Trichlorophenol	0.74	196(100), 198(92), 200(26)
4-Chloro-m-cresol	0.83	142(100), 107(80), 144(32)
2,4-Dinitrophenol	1.03	184(100), 63(59), 154(53)
4,6-Dinitro-o-cresol	1.04	198(100), 182(35), 77(28)
Pentachlorophenol	1.15	266(100), 264(62), 268(63)
4-Nitrophenol	1.70	65(100), 139(45), 109(72)

a/ Column: 1.2 m x 2 mm ID glass; 1% SP-1240 DA on 100/120 Supelcoport; He at 30 ml/min.
Program: 85°C for 4 min, then 10°C/min to 200°C and hold for 15 min.

007506

Table 2.5. Base-Neutral Compounds

Compound Name	RRT[a] D-10-Anthracene	Characteristic EI Ions (Rel. Int.)
1,3-Dichlorobenzene	0.31	146(100), 148(64), 113(12)
1,4-Dichlorobenzene	0.33	146(100), 148(64), 113(11)
Hexachloroethane	0.35	117(100), 199(61), 201(99)
1,2-Dichlorobenzene	0.35	146(100), 140(64), 113(11)
Bis(2-chloroisopropyl) ether	0.37	45(100), 77(19), 79(12)
Hexachlorobutadiene	0.48	225(100), 223(63), 227(65)
1,2,4-Trichlorobenzene	0.49	74(100), 109(80), 145(52)
Napthalene	0.51	128(100), 127(10), 129(11)
Bis(2-chloroethyl) ether	0.55	93(100), 63(99), 95(31)
Hexachlorocyclopentadiene	0.59	237(100), 235(63), 272(12)
Nitrobenzene	0.45	77(100), 123(50), 65(15)
Bis(2-chloroethoxy)methane	0.50	93(100), 95(32), 123(21)
2-Chloronaphthalene	0.68	162(100), 164(32), 127(31)
Acenaphthylene	0.75	152(100), 153(16), 151(17)
Acenaphthene	0.77	154(100), 153(95), 152(53)
Isophorone	0.47	82(100), 95(14), 138(18)
Fluorene	0.85	166(100), 165(80), 167(14)
2,6-Dinitrotoluene	0.81	165(100), 63(72), 121(23)
1,2-Diphenylhydrazine[b]	0.87	77(100), 93(58), 105(28)
2,4-Dinitrotoluene	0.85	165(100), 63(72), 121(23)
N-Nitrosodiphenylamine[c]	0.89	169(100), 168(71), 167(50)
Jexacj;prpbemzeme	0.92	284(100), 142(30), 249(24)
4-Bromophenyl phenyl ether	0.92	248(100), 250(99), 141(45)
Phenanthrene	1.00	178(100), 179(16), 176(15)
Anthracene	1.00	178(100), 179(16), 176(15)
Dimethyl phthalate	0.78	163(100), 164(10), 194(11)
Diethyl phthalate	0.87	149(100), 178(25), 150(10)
Fluoranthene	7.18	202(100), 101(23), 100(14)
Pyrene	1.22	202(100), 101(26), 100(17)
Di-n-butyl phthalate	1.09	149(100), 150(27), 104(10)
Benzidine	1.27	184(100), 92(24), 185(13)
Butylbenzyl phthalate	1.34	149(100), 91(50)
Chrysene	1.40	229(100), 229(19), 226(23)
Di-(2-ethylhexyl) phthalate	1.37	149(100), 167(31), 279(26)
Benzo(a)anthracene	1.41	228(100), 229(19), 226(19)
Di-n-octylphthalate	1.41	149(100), 167, 279
Benzo(b)fluoranthene	1.43	252(100), 253(23), 125(15)
Benzo(k)fluoranthene	1.43	252(100), 253(23), 125(16)
Benzo(a)pyrene	1.50	252(100), 253(23), 125(21)
Indeno(1,2,3-cd)pyrene	1.86	276(100), 138(28), 277(27)

Table 2.5 (Concluded)

Compound Name	RRT D-10-Anthracene	Characteristic EI Ions (Rel. Int.)
Benzo(g,h,i)perylene	1.98	276(100), 138(37), 277(25)
N-Nitrosodimethylamine	0.15	42(100), 74(88), 44(21)
N-Nitrosodi-n-propylamine	0.42	130(22), 42(64), 101(12)
4-Chlorophenyl phenyl ether	0.85	204(100), 206(34), 141(29)
3,3'-Dichlorobenzidine	1.45	252(100), 254(66), 126(16)
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1.33	322(100), 320(90), 59(95)
Bis(chloromethyl)ether	--	45(100), 49(14), 51(5)
Deuterated anthracene (d10)	1.00	188(100), 94(19), 80(18)

a/ 1% SP-2250 on 100/120 mesh Supelcoport in a 1.8 m x 2 mm ID glass column; He at 30 ml/min. Program: 50°C for 4 min, then 10°C/min to 260°C and hold for 15 min.

b/ Elutes as azobenzene.

c/ Elutes as diphenylamine.

007508

Table 2.6. Pesticides

Compound Name	RRT[a] D-10-Anthracene	Characteristic EI Ions (Rel. Int.)
β-endosulfan	0.47	201(100), 283(48), 278(30)
α-BHC	0.94	183(100), 109(86), 181(91)
γ-BHC	1.00	183(100), 109(86), 181(91)
β-BHC	1.03	181(100), 183(93), 109(62)
Aldrin	1.05	66(100), 220(11), 263(73)
Heptachlor	1.06	100(100), 272(60), 274(46)
Heptachlor epoxide	1.13	355(100), 353(79), 351(60)
α-Endosulfan	1.14	201(100), 283(48), 278(30)
Dieldrin	1.18	79(100), 263(28), 279(22)
4,4'-DDE	1.20	246(100), 248(64), 176(65)
4,4'-DDD	1.22	235(100), 237(76), 165(93)
4,4'-DDT	1.27	235(100), 237(72), 165(59)
Endrin	1.30	81(100), 82(61), 263(70)
Endosulfan sulfate	1.30	272(100), 387(75), 422(25)
δ-BHC	1.04	183(100), 109(86), 181(90)
Chlordane	1.05-1.26	373(19), 375(17), 377(10)[b]
Toxaphene	1.12-1.35	(231, 233, 235)[c]
PCB-1242	0.86-1.14	(224, 260, 294)[c]
PCB-1254	1.09-1.30	(294, 330, 362)[c]

a/ 1% SP-2250 on 100/120 mesh Supelcoport in a 1.8 m x 2 mm ID glass column; He at 30 ml/min. Program: 50° for 4 min, then 10°C/min to 260° and hold for 15 min.

b/ These three ions are characteristic for the α and γ forms of chlordane. No stock should be set in these three for other isomers.

c/ These ions are listed without relative intensities since the mixtures they represent defy characterization by three masses.

007509

Table 2.7. Representative Purgeable Compounds for Recovery Studies

Benzene
Carbon tetrachloride
Chlorobenzene
Chloroform (trichloromethane)
1,2-Dichloroethane
1,1-Dichloroethane
Ethyl benzene
Tetrachloroethane
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Chloroethane

Table 2.8. Representative Semivolatile Compounds for Recovery Studies

Acenaphthylene
Benzidine
Benz[a]pyrene
Bis(2-chloroethyl) ether
Bis(2-chloroisopropyl) ether
Bis(2-ethylhexyl)phthalate
Butylbenzylphthalate
3,3'-Dichlorobenzidine
2,4-Dichlorophenol
2,4-Dimethylphenol
2,6-Dinitrotoluene
Fluoranthene
Hexachloroethane
N-Nitrosodimethylamine
1,4-Dichlorobenzene
Pentachlorophenol
Phenol
Dieldrin
α-BHC
p,p'-DDE
Heptachlor

APPENDIX I

Table A-1. Elution Order and Fortification Detection Limits of Volatile Priority Pollutants[a/]

Compound	RRT[b/]	Detection limit[c/] (ng)
Chloromethane	0.152	50
Dichlorodifluoromethane	0.172	800
Bromomethane	0.181	800
Vinyl chloride	0.186	75
Chloroethane	0.204	800
Methylene chloride	0.292	20
Trichlorofluoromethane	0.372	150
1,1-Dichloroethylene	0.380	50
Bromochloromethane (IS)	0.457	-
1,1-Dichloroethane	0.469	75
Trans-1,2-dichloroethylene	0.493	50
Chloroform	0.557	50
1,2-Dichloroethane	0.600	50
1,1,1-Trichloroethane	0.672	50
Carbon tetrachloride	0.684	50
Bromodichloromethane	0.750	75
Bis-chloromethyl ether	0.760	d/
1,2-Dichloroporpane	0.818	50
Trans-1,3-dichloropropene	0.847	50
Trichloroethylene	0.867	50
Dibromochloromethane	0.931	50
Cis-1,3-dichloropropene	0.913	50
1,1,2-Trichloroethane	0.913	50
Benzene	0.937	5
2-Chloroethylvinyl ether	0.992	50
2-Bromo-1-chloropropane (IS)	1.000	-
Bromoform	1.115	50
1,1,2,2-Tetrachloroethene	1.262	50
1,1,2,2-Tetrachloroethane	1.281	50
1,4-Dichlorobutane (IS)	1.312	-
Toluene	1.341	5
Chlorobenzene	1.489	10
Ethylbenzene	1.814	5
Acrolein	Unknown	500
Acrylonitrile	Unknown	250

a/ These data were obtained under the following conditions: GC column - stainless steel, 8-ft long x 0.1 in. I.D. packed with Carbopack C (60/80 mesh), coated with 0.2% Carbowax 1500; carrier flow - 30 ml/min; oven temperature - initial 60°C held for 3 min, programmed 8°C/min to 160°C and held until all compounds eluted.

b/ Retention times relative to 2-bromo-1-chloropropane with an absolute retention time of 829 sec.

c/ Detection limit for fortification protocol assuming a 1 ml sample aliquot of a sludge with 5% solids content actual detection limits may vary slightly.

d/ Half-life of approximately 10 sec in aqueous mixtures.

Table A-2. Fortification Detection Limits for Base, Neutral, Pesticide, and Acid Extractable Organic Priority Pollutant Compounds

Detection Limit Range[a/] ng/ml	Compound
< 10	Naphthalene
	Fluorene
	Di-n-butylphthalate
	Fluoranthene
	Pyrene
	Bis(2-ethylhexyl)phthalate
	Acenaphthylene
	Diethylphthalate
	Benzo(k)fluoranthene
	Bis(2-chloroisopropyl)ether
	1,2-diphenylhydrazine
	Phenanthrene/anthracene
10 - 20	2-Chloronaphthalene
	Acenaphthalene
	2,6-Dinitrotoluene
	Butylbenzylphthalate
	Benzo[a]pyrene
	1,2,4-Trichlorobenzene
	Dimethylphthalate
	Di-n-octylphthalate
	4-Chlorophenylphenylether
	Hexachlorobenzene
	Benzidine
	3,3'-Dichlorobenzidine
	4,4'-DDE
	4,4'-DDT
	Toxaphene
	Chrysene/benzo[a]anthracene
20 - 30	m-Dichlorobenzene
	> o-Dichlorobenzene<p-dichlorobenzene
	Hexachlorobutadiene
	N-Nitrosodiphenylamine
	4-Bromophenylphenylether
	Dibenzo[a,b]anthracene
	Hexachloroethane
	Benzo[g,h,i]perylene
	Aldrin
	Phenol

Table A-2 (Concluded)

Detection Limit Range ng/ml	Compound
30 - 40	Bis(2-chloroethyl)ether
	α-BHC
	γ-BHC
	Endrin
	Heptachlor
	2-Chlorophenol
40 - 50	2,4-Dinitrotoluene
	N-Nitroso-di-n-propylamine
	δ-BHC
	2,4-Dimethylphenol
	2,4-Dichlorophenol
50 - 100	Nitrobenzene
	Bis(2-chloroethoxy)methane
	Hexachlorocyclopentadiene
	β-BHC
	Heptachlor epoxide
	Dieldrin
	2-Nitrophenol
	Trichlorophenol
	p-Chloro-m-cresol
~ 230 } 200	Pentachlorophenol
~ 240 }	4,6-Dinitro-o-cresol
~ 310 } 300	p-Nitrophenol
~ 340 }	Isophorone
~ 630 - 600	2,4-Dinitrophenol

a/ Detection limit based on standard responses and a minimum count of 1,000 for compound identification. Detection limits are for the original analyte concentration in sludge and presumes use of this protocol.